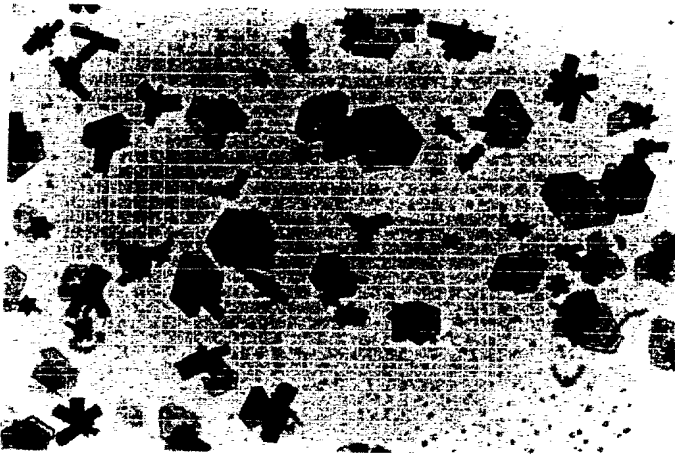




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C01B 31/00	A1	(11) International Publication Number: WO 92/04279 (43) International Publication Date: 19 March 1992 (19.03.92)
(21) International Application Number: PCT/US91/05983 (22) International Filing Date: 21 August 1991 (21.08.91) (30) Priority data: 575,254 30 August 1990 (30.08.90) US 580,246 10 September 1990 (10.09.90) US (71) Applicant: RESEARCH CORPORATION TECHNOLOGIES, INC. [US/US]; 6840 East Broadway Boulevard, Tucson, AZ 85710 (US). (72) Inventors: HUFFMAN, Donald, R. ; 6633 E. Koralee, Tucson, AZ 85710 (US). KRATSCHMER, Wolfgang ; Schwäbisch Hall Str. 9, D-6901 Gaiberg (DE).		(74) Agent: SCOTT, Anthony, C.; Scully, Scott, Murphy & Presser, 400 Garden City Plaza, Garden City, NY 11530 (US). (81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>
(54) Title: NEW FORM OF CARBON  (57) Abstract C ₆₀ and C ₇₀ carbon atom compounds are prepared by evaporating graphite in an inert quenching gas. The vapor of carbon is collected and is selectively extracted with an organic non-polar solvent.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland			SN	Senegal
CI	Côte d'Ivoire	KR	Republic of Korea	SU ⁺	Soviet Union
CM	Cameroon	LI	Liechtenstein	TD	Chad
CS	Czechoslovakia	LK	Sri Lanka	TG	Togo
DE*	Germany	LU	Luxembourg	US	United States of America
DK	Denmark	MC	Monaco		

⁺ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

NEW FORM OF CARBON

1

This invention relates to new forms of carbon as well as methods for the production and recovery thereof from carbon sources.

5

In 1985, Kroto et al. postulated the existence of a highly stable molecule composed of 60 carbon atoms based solely on mass spectroscopic analysis of vaporized graphite (H.W. Kroto, et al., Nature, Vol. 318, 162, 14 November 1985). More specifically, all that was observed was a peak in the mass spectra of said carbon vapor. However, Kroto et al. did not isolate any of said compound.

10

A model for this compound was proposed in which 60 carbon atoms are placed at the vertices of a truncated icosahedron forming a perfect "soccerball" structure. Subsequent thereto, many publications have strengthened the evidence for the existence of this molecule. The 60 carbon atom compound (hereinafter C_{60}) was presumably produced in situ for the spectroscopic determination reported in these publications. Yet, to date, no one has been successful in verifying the existence of this molecule since no one has been successful in isolating the molecule in measurable amounts. Thus, no processes for producing recoverable amounts of this new compound have been described to the present time.

20

25

In the aforesaid publication by Kroto, et al., the authors proposed many uses for the new substance, C_{60} if it could be produced in quantity such as C_{60} transition metal compounds, e.g., $C_{60}Fe$; or halogenated species like $C_{60}F_{60}$ which might be a super lubricant; molecules including oxygen and lanthanum in the C_{60} interior; C_{60} would provide a topologically novel

30

35

1 aromatic nucleus for new branches of organic and
inorganic chemistry; and C_{60} being especially stable and
symmetrical provides possible catalyst and/or
intermediate in modelling prebiotic chemistry.

5 Another form of carbon containing 70 carbon atoms
(C_{70}) has also been postulated (Kroto, Chemistry in
Britain, 40-45 (1990), Kroto, Science, 1139-1145 (1988)).
Like the (C_{60}) to date, no one has been successful in
verifying the existence of the C_{70} . Heretofore, no one
10 has been successful in obtaining the molecule in any
appreciable amounts.

A process has now been developed for the
production of recoverable amounts of C_{60} and C_{70} . The
15 present invention relates to a method of producing C_{60} and
 C_{70} compounds which comprises evaporating graphite in an
atmosphere of an inert quenching gas at effective pressures
in an evacuated reactor, collecting the quenched carbon
product produced therefrom and contacting the quenched carbon
20 product with an extracting non-polar organic solvent
under effective conditions to separate the C_{60} and C_{70}
compounds therefrom. The present new process is accomplished
by evaporating carbon rods in an atmosphere of an inert
25 quenching gas maintained at reduced pressure in a reactor
therefor. This process produces a sooty carbon product
which is graphitic carbon including a few percent of C_{60}
and low levels of C_{70} which are recoverable from the
product. However, an increase in the fraction of C_{70}
30 molecules can be produced if the pressure is raised to
greater than atmospheric pressures.

The recovery process is preferably accomplished
by selective extraction of C_{60} and C_{70} with non-polar
organic solvents from the sooty graphitic carbon.
35

1 The processes of the present invention produces
C₆₀ and C₇₀ in recoverable amounts and permits realization
of the proposed uses described hereinbefore.

 In the accompanying figures, Fig. 1 is a
5 micrograph of typical crystals of the 98% C₆₀, 2% C₇₀
material showing thin platelets, rods and stars of
hexagonal symmetry.

 Fig. 2 is a x-ray diffraction of a
microcrystalline powder of the 98% C₆₀, 2% C₇₀ solid
10 material. Inset at upper left is a single crystal
electron diffraction pattern indexed with Miller indices
compatible with the x-ray pattern, taken on a thin
platelet as in Figure 1 with the electron beam
perpendicular to the flat face.

15 Fig. 3 is an infrared absorption spectrum of an
approximately 2 micrometer thick coating of the 98% C₆₀,
2% C₇₀ material on a silicon substrate, referenced to a
clean silicon substrate. Absorption is given as optical
density = $\log_{10} 1/T$, where T is transmission. Apparent
20 negative absorptions are due to the coating acting in part
as a non-reflecting layer.

 Fig. 4 is a visible-ultraviolet absorption
spectrum of an approximately 0.1 micrometer thick coating
of the 98% C₆₀, 2% C₇₀ material on quartz. Shown at the
25 bottom are positions and relative oscillator strengths for
allowed transitions calculated for the C₆₀ molecule by
Larsson, et al.

 The first step in the production of C₆₀ and C₇₀
molecules is vaporizing carbon from any source containing
30 carbon in its various forms; e.g., graphite, amorphous and
glassy carbon. It is preferred that this vaporization
takes place in an evacuated reactor (e.g., a bell jar).
The carbon is vaporized by heating in the presence of an
inert quenching gas. The carbon vapor is nucleated in the
35 presence of the inert quenching gas to form smoke
particles.

1 In the production of C_{60} and C_{70} , any procedure
for vaporizing carbon can be used, although the preferred
method relies on the use of a high intensity electrical
current with graphite rods as electrodes. These rods are
5 constructed to permit vaporization of carbon at the tip
of the rod to produce a high density vapor of carbon.
For best results, the end of one of the rods is reduced
in diameter so that the vaporization occurs at the
reduced tip. The rods can be prepared using any of the
10 various forms of carbon, such as graphite, amorphous and
glassy carbon.

The inert quenching gas can be any of the usual
inert gases such as the noble gas. Argon and helium are
preferred, the latter being most preferred. Other inert
15 gases commonly employed to provide a non-reactive
atmosphere can also be used as quenching gas.

The amount of C_{60} and C_{70} produced from this
carbon source is dependent upon the pressure of the
quenching gas. At lower pressures relatively pure C_{60}
20 molecules can be produced in high yield with minor
concentrations of C_{70} . For the production of
predominantly C_{60} molecules, the pressure at which the
quenching gas is maintained should be subatmospheric and
preferably about 50-400 torr. Especially preferred is a
25 pressure of approximately 100 torr. The use of any lower
pressure may result in reduced yield of C_{60} .

However, as the pressure is raised, the ratio
of $C_{70}:C_{60}$ is also increased.

30 If the pressure is increased to at least two
atmospheres, the greatest percentage of C_{70} product is
formed. Theoretically, the pressure can be raised to any
level just below the point where the reactor would

1 explode from the increased pressure. However, at the
higher pressures, the yield of the overall product (C_{60}
and C_{70}) is reduced even though the ratio of $C_{70}:C_{60}$ is
also increased. Therefore, as a practical consideration,
5 the pressure of the quenching gas should not be greater
than 10 atmospheres. The preferred pressure for
maximizing the amount of C_{70} produced is 2-3 atmospheres.

The produced quenched vapor of carbon, i.e.,
10 the smoked particles coats the internal surface of the
reactor and of collecting substrates as black soot.
These collecting surfaces are inert to the vaporized
carbon. They can be transparent and/or coated with an
inert metal. Examples include glass, or gold coated
15 glass surfaces and the like. These collecting surfaces
are located in the reactor in the path of the carbon
smoke. The black coating can be removed by any suitable
means, e.g., by scraping the solids from the coated
surfaces. The C_{60} and C_{70} molecules can be removed from
20 this collected quenched product by contacting said
quenched product with an extracting solvent. In other
words, the black soot is placed in a container containing
the extracting solvent, or the extracting solvent is
poured onto the black soot placed in a container. In
25 either case, the C_{60} and C_{70} molecules become dissolved in
the solvent, while the remainder of the black soot
remains insoluble. The insoluble material is separated
from the solution containing the C_{60} and C_{70} molecules,
e.g., by decanting, or by filtration, and the like.

30 Suitable solvents include non-polar organic
solvents, such as the alkanes containing 5-10 carbon
atoms (e.g. pentanes, hexanes, heptanes, octanes),
benzene and alkyl-benzenes (e.g. toluene, xylene), carbon
disulfide, carbon tetrachloride, naphtha, 1,1,1-

1 trichloroethane, and the like. Simple solubility
determinations using classical laboratory methods will
5 permit selection of other suitable solvents. The
preferred solvents are carbon disulfide, benzene, carbon
tetrachloride and toluene. Especially preferred are
benzene, carbon tetrachloride and carbon disulfide.

The product obtained contains a mixture of C_{60}
and C_{70} . As described hereinabove, the amounts of C_{60}
10 and C_{70} present is dependent upon the pressure used. If
subatmospheric pressures are used, such as 50-400 torr,
the product is predominately pure C_{60} with a minor amount
of C_{70} present. Thus, when the collected product is
dispersed in the extracting solvent, the product obtained
15 is a mixture of C_{60} and C_{70} . For example, when the
pressure is 100 torr, the product formed is about 98% C_{60}
and about 2% C_{70} . This product can be separated from the
organic solvent solution by standard methods as by
evaporation of the solvent or by dilution of the solvent
20 solution with a non-solvent for C_{60} . The product can be
crystallized by careful evaporation of the organic
solvent or by sublimation procedures.

In a preferred embodiment of producing C_{60} and
 C_{70} , pure graphite rods are vaporized by passing high
25 electrical current (either dc or ac) through narrowed
tips of graphite rods. Electron beam, laser and RF
heating can be used in lieu of electrical heating. This
is done in a reactor (such as a bell jar) that has been
evacuated, purged and filled with inert gas at or
30 preferably below atmospheric pressure, e.g., pressures
ranging from about 50 to about 400 torr. and even higher.
The graphite rods are typically 1/4 inch in diameter with

1 about 1 cm length of one rod reduced in diameter to about
5 mm. The electrical heating vaporizes the constricted
tip of the graphite rod producing a high density vapor of
carbon, which quickly condenses into a smoke consisting
5 of very fine particles (of the order of 0.1 microns) of
graphitic carbon with an admixture of a few percent of
the desired C_{60} molecule. At this point in the process
there is a heavy black coating on collecting substrates
and/or on the walls of the chamber which can be easily
10 scraped off for the recovery step.

For recovery, the sooty product is treated with
benzene to provide a brownish-red solution. After
separation of the undissolved graphitic carbon, the
benzene solution is evaporated to obtain microcrystalline
15 product. Alternatively, the product can be sublimed from
the sooty carbon at 300° to 400°C. and the sublimation
product obtained by condensation on a conventional
substrate.

When the pressure of inert quenching gas is 100
20 torr, the product formed is 98% C_{60} and 2% C_{70} . This
product, as obtained from the solvent extract of the
sooty graphitic carbon, is a dark brown to black
crystalline material. When obtained by sublimation in
vacuum or inert atmosphere, the product is obtained as a
25 brown to gray coating depending on thickness.

On analysis by mass spectroscopy, the spectrum
clearly shows a strong peak at mass 720 amu (i.e., the
mass of C_{60}) and a clean peak at 840 amu (i.e., the mass
of C_{70}). Significant differences in the spectra occur
30 only in the abundances in the mass domain lower than 300
amu. Most of these differences seem to originate from
the different ionization techniques in the mass
spectrometer and from the different kinds of sample
desorption. So far, the cleanest mass spectra have been
35

1 obtained when the material was evaporated and ionized in
the vapor phase by electrons. In such spectra the mass
range above 40 amu is dominated by the C_{60} mass along
with its expected isotope lines. The only other large
5 mass found in any abundance corresponds to C_{70} , with a
ratio of C_{70} to C_{60} of about .02.

Studies by optical microscopy of the C_{60}
material which is left after evaporating the benzene
solution show a variety of what appear to be crystals --
10 mainly rods, platelets, and star-like flakes. Figure 1
shows a micro-photograph of such a crystal assemblage.
All crystals tend to exhibit six-fold symmetry. In
transmitted light they appear red to brown in color; in
reflected light the larger crystals have a metallic
15 appearance, whereas the platelets show interference
colors consistent with an index of refraction of about 2.

The platelets can be rather thin and thus are ideally
suited for electron diffraction studies in an electron
20 microscope. (See the insert in Figure 2).

In order to determine if the C_{60} molecules form
a regular lattice electron, x-ray diffraction studies on
the individual crystals and on the powder were carried
out. A typical X-ray diffraction pattern of the purified
25 C_{60} powder is shown in Figure 2. To aid in comparing the
electron diffraction results with the X-ray results the
electron diffraction pattern is inserted into the corner
of Figure 2. From the hexagonal array of diffraction
spots indexed as shown in the Figure, a d-spacing of 8.7
30 Å was deduced corresponding to the (100) reciprocal
lattice vector of a hexagonal lattice. The most obvious
correspondence between the two types of diffraction is
between the 5.01 Å peak of the X-ray pattern and the

- 1 (100) spot of the electron diffraction pattern, which
 gives a spacing of about 5.0 Å. Assuming that the C₆₀
 molecules are behaving approximately as spheres stacked
 in a hexagonal close packed lattice with a c/a ratio of
 5 1.633, d-spacings can be calculated. The results are
 shown in Table I.

Table I: X-Ray Diffraction Results and
 Assignments For a Hexagonal Lattice Using
 10 $a = 10.02 \text{ Å}$, $c = 16.36 \text{ Å}$

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{2}{c^2}$$

15	Measured 20 (degrees)	Measured d-spacing (Å)	Calculated d-spacing (Å)	Assignment (hkl)
	10.2 shoulder	8.7	8.68	(100)
20	10.81	8.18	8.18	(002)
			7.67	(101)
	17.69	5.01	5.01	(110)
	20.73	4.28	4.27	(112)
	21.63	4.11	4.09	(004)
25	28.1	3.18	3.17	(114)
	30.8	2.90	2.89	(300)
	32.7	2.74	2.73	(006)

The values derived from this interpretation are
 $a = 20.02 \text{ Å}$ and $c = 16.36 \text{ Å}$. The nearest neighbor
 30 distance is thus 10.02 Å. For such a crystal structure
 the density is calculated to be 1.678 g/cm³, which is
 consistent with a value of 1.65 +/- .05 determined by
 suspending crystal samples in aqueous GaCl₃ solutions of

1 known densities. Although the agreement shown in Table 1
is good, the absence of the characteristically strong
(101) diffraction in hcp and the broad continuum in
5 certain regions suggest a less than perfect crystalline
order. Furthermore, X-ray diffraction patterns obtained
on carefully grown crystals up to 500 micrometers in size
with well developed faces yielded no clear spot pattern
(in contrast to the electron diffraction pattern on
10 micron-size crystals). It thus appears that these larger
crystals do not exhibit long range periodic order in all
directions.

A likely explanation for the unusual
diffraction lies in the disordered stacking arrangement
of the molecules in planes normal to the c-axis. It is
15 well known that the position taken by spheres in the
third layer of stacking determines which of the
close-packed structures occurs, the stacking arrangement
in fcc being ABCABC while that in hcp is ABABAB. If the
stacking sequence varies, the X-ray lines due to certain
20 planes will be broadened by the disorder while other
lines will remain sharp. Such disordered crystalline
behavior was observed long ago in the close packed
structure of cobalt, where X-ray diffraction lines such
as (101), (102) and (202) were found to be substantially
25 broadened due to the stacking disorder. Reflections from
planes such as (002) remain sharp since these planes have
identical spacings in both fcc and hcp structures. A
general expression for which peaks are broadened by this
kind of disorder have been given in terms of Miller
30 indices (h,k,l) as $h - k = 3t \pm 1$, $l \neq 0$, where t is an
integer. None of these broadened reflections are
apparent in the X-ray pattern of Figure 2. This may
explain the weakness of the characteristically strong

1 (101) peak. Whether or not this stacking disorder is
related to the presence of the possibly elongated C_{70}
molecules is yet to be determined.

5 In small crystals at least, the C_{60} molecules
appear to be assembling themselves into a somewhat
ordered array as though they are effectively spherical,
which is entirely consistent with the soccer ball
hypothesis for their structure. The additional diameter
over the calculated 7.1 \AA value for the carbon cage
10 itself must represent the effective van der Waals
diameter set by the repulsion of the pi electron clouds
extending outward from each carbon atom. Scanning
tunnelling spectroscopy of the C_{60} molecules clearly
shows the spherical nature of the C_{60} molecules.

15 Some scanning tunnelling microscope images of a
carbon sample prepared in accordance with the procedure
described hereinabove at pressures of helium at 100 torr
show a spherical molecule of twice the diameter of the
 C_{60} molecules. This is evidence of the existence of a
20 caged molecule containing 240 carbon atoms or a C_{240}
molecule.

Samples were prepared for spectroscopy by
subliming pure material onto transparent substrates for
transmission measurements. Depending on the pressure of
25 helium in the sublimation chamber, the nature of the
coatings can range from uniform films (at high vacuum) to
coatings of C_{60} smoke (i.e., sub-micron microcrystalline
particles of solid C_{60}) with the particle size depending
to some extent on the pressure.

30 Figure 3 shows the transmission spectrum of an
approximately 2 micrometer thick C_{60} coating on a silicon
substrate. The infrared bands show the four most intense
lines at $1429, 1183, 577, \text{ and } 528 \text{ cm}^{-1}$, with no

1 underlying continuum remaining from the soot. In early
tries at purifying C₆₀ material, the infrared spectrum
showed a strong band in the vicinity of 3.0 micrometers,
which is characteristic of a CH stretching mode. After
5 much effort, this contaminant was successfully removed by
washing the soot with ether and using distilled benzene
in the extraction. The spectrum in Figure 3 was obtained
when the material cleaned in such a manner was sublimed
under vacuum onto the substrate. The spectrum shows very
10 little indication of CH impurities.

The presence of only four strong bands is what
is expected for the free, truncated icosahedral molecule
with its unusually high symmetry. Also present are a
number of other weak infrared lines which may be due to
15 other causes, among which may be absorption by the C₇₀
molecule or symmetry breaking produced, for example, by
isotopes other than C¹² in the C₆₀ molecule or by mutual
interaction of the C₆₀ molecules in the solid.
Noteworthy, are weaker features at about 2330 and 2190
20 cm⁻¹ which are located in the near vicinity of the free
CO₂ and CO stretching modes. This may imply some
attachment of CO₂ or CO to a small fraction of the total
number of C₆₀ molecules. Another noteworthy effect can
be observed in the feature at 675 cm⁻¹, which is weak in
25 the thin film samples but almost as strong as the four
main features in the crystals. This vibrational mode may
be of solid state rather than molecular origin.

Figure 4 shows an absorption spectrum taken on
a uniform film coated onto a quartz glass substrate. The
30 ultraviolet features are no longer obscured by the
graphitic carbon background as in our previous spectra.
Broad peaks at 216, 264 and 339 nm dominate the spectra.
Weaker structures show up in the visible, including a

1 plateau with ends at about 460 and 500 nm and a very weak
peak near 625 nm. At the bottom of Figure 4 are shown
positions and relative oscillator strengths taken from
Larsson, et al. (Chem. Phys. Lett. 137, 501-504)
5 calculated for the C_{60} molecule. This reference also
shows a variety of forbidden bands with the lowest energy
ones in the vicinity of 500 nm. There seems to be a
rough correspondence between the present measurements on
thin films and the allowed transitions predicted for the
10 molecule. There was no band at 386 nm in our films of
 C_{60} , a disclosed by Heath, et al. (J. Chem. Phys. 87,
4236-4238 (1987)) using a laser depletion spectroscopy
method and attributed to the C_{60} molecule. Quite similar
spectra to that in Figure 4 have been recorded for
15 microcrystalline coatings deposited at helium pressures
of 100 torr, for example. The peaks occur at the
slightly shifted positions of 219, 268, and 345 nm.

The C_{70} molecule is larger than the C_{60}
molecule. The C_{70} molecule shows a molecular ion peak at
20 840 amu. Furthermore, a noticeable peak in the
ultraviolet spectrum of the C_{70} molecule taken on a
uniform film coated onto a quartz glass substrate is
exhibited at about 216 nm. This is a broad peak.
Suprisingly, it appears that the C_{70} molecule is more
25 stable than C_{60} .

Thus, using the procedures described
hereinabove, at quenching pressures of less than 1
atmospheric pressure and especially at pressures of
50-400 torr, a product is produced which is predominantly
30 C_{60} and contains minor amounts of C_{70} . The C_{60} product
can be used or can be further purified.

Further purification and separation of C_{60} and
 C_{70} can be made by many conventional techniques known to

1 one skilled in the art, e.g., fractional crystallization,
column chromatography, capillary electrophoresis, HPLC,
preparative thin-layer chromatography, and the like.

5 Because the molecular figuration of C_{60} and C_{70}
are different, the attractive intermolecular forces are
different which allows for the two molecules to be
readily separated.

10 Furthermore, the solubility of C_{60} and C_{70} in
pure solvents and mixed solvents are also different from
each other, which also makes the two compounds separable
by using conventional techniques known to one skilled in
the art, such as crystallization, extraction, and the
like.

15 For example, pure C_{60} and pure C_{70} molecules
can be isolated as follows. The black sooty mixture of
 C_{60} and C_{70} which is produced according to the procedure
described hereinabove is placed in the extracting
solvent, such as benzene. The insoluble residue is
removed and the resulting benzene solution containing C_{60}
20 and C_{70} molecules is concentrated. The C_{60} and C_{70}
solution is added to a packed column with an adsorbent,
such as alumina. The column is eluted with an eluent
such as benzene or a mixture of benzene and toluene.
Various fractions of set volume e.g., 10 mL, are
25 collected. The eluent i.e., the solvent is removed from
each fraction such as by evaporation to dryness. The
fractions with product will contain microcrystals, the
identity of which can be confirmed by spectroscopy, e.g.,
mass spectroscopy.

30 Thus, the process of the present invention can
produce a product which is predominantly C_{60} , which, if
desired, can be further purified by the purification and
separation techniques described hereinabove.

35

1 Furthermore, the present invention contemplates
two different variations of the procedure described
hereinabove to make C_{70} molecules. First, if
subatmospheric pressures of quenching gases are used in
5 the initial step, small amounts of C_{70} are produced,
which can be separated from the C_{60} molecules using the
purification techniques described hereinabove. However,
if the pressure of the quenching gas is raised to at
least 2 atmospheres, after separation and purification, a
10 greater percentage of substantially pure C_{70} would be
produced from each vaporization of carbon.

The present new products, C_{60} , C_{70} , or mixtures
thereof have the similar utilities as graphite. However,
they are particularly valuable for forming products of a
15 higher order of stability than those formed from
graphitic carbon, and can be processed into formed or
molded products such as C_{60} fibers, C_{70} fibers, or
mixtures thereof using standard processing techniques.
In this regard, free-flowing, particulate C_{60} and C_{70} are
20 of special value particularly for use in producing molded
products, especially those extended in at least one
direction. C_{60} and C_{70} are also useful for producing a
low temperature C_{60} vapor (300°-400°C.) and C_{70} vapor of
the respective molecules to produce low temperature
25 atomic and molecular beams of carbon which is not now
possible using graphite as the carbon source. Further,
the synthesis of compounds such as $C_{60}H_{60}$ and $C_{60}F_{60}$ can
be accomplished by introducing hydrogen and fluorine,
respectively, into a reactor containing C_{60} vapor.
30 Furthermore, the C_{60} product and the C_{70} product may be
used as an industrial paint pigment or as a lubricant.
Moreover, since the C_{60} and C_{70} molecule are hollow, they
could be used for binding and/or storing molecules e.g.,
toxic material.

1

EXAMPLE 1

5 C_{60} -containing carbon dust was produced in a conventional bell-jar carbon evaporator which was first evacuated to 10^{-4} torr by either an oil diffusion pump or a turbo pump, both equipped with liquid nitrogen traps, and then filled with an inert quenching gas. Helium and argon were used at pressures ranging up to 400 torr. Then graphite rods (as previously described herein) were
10 evaporated using a current of about 100 amps (either AC or DC).

The smoke which formed in the vicinity of the evaporating carbon rods was collected on substrates which were placed within 5 cm to 10 cm of the evaporating
15 carbon rods.

The evaporator was opened after a cool down period of 10-30 min. and the carbon dust samples removed by scraping substrate surfaces and the internal surfaces of the bell-jar. After washing with ether, the collected
20 dust samples were then extracted with benzene to produce a wine-red to brown solution. On evaporation of the solution, C_{60} was obtained as a microcrystalline residue.

The crystals were sublimed by heating in vacuo or in a quenching inert gas to 400°C. and collected on a
25 substrate. The sublimed product was brown to gray in color.

In powder form, the present new carbon allotrope is brownish-red.

30

35

1

EXAMPLE 2

The procedure of Example 1 is repeated except, in the original step, the graphite rods are evaporated at 2 or more atmospheres of helium pressure in the chamber.

5

The product obtained from this procedure contains a greater percentage of C₇₀ than does the product in Example 1.

10

15

20

25

30

35

1

EXAMPLE 3

Pure C₆₀ and pure C₇₀ are obtained as follows:

The C₆₀ and C₇₀ mixtures prepared in either Examples 1 or 2 are dissolved in benzene and added to an alumina column. Using benzene as the eluent, the fractions are collected and each elute fraction is evaporated to dryness. The presence of C₆₀ or C₇₀ in the fraction can be determined by taking mass spectroscopy thereof.

10

15

20

25

30

35

1 The above embodiments and examples are given to
illustrate the scope and spirit of the instant invention.
These embodiments and examples are within the
contemplation of the present invention. Therefore, the
5 present invention should be limited only by the appended
claims.

10

15

20

25

30

35

1 WHAT IS CLAIMED IS:

1. A method of producing C_{60} and C_{70} compounds which comprises evaporating graphite in an atmosphere of an inert quenching gas at effective pressures in an evacuated reactor, collecting the quenched carbon product produced therefrom and contacting the quenched carbon product with an extracting non-polar organic solvent under effective conditions to separate the C_{60} and C_{70} compounds therefrom.

2. The method according to Claim 1 wherein the quenched carbon is collected on a collecting substrate.

3. The method according to Claim 1 or 2 wherein the C_{60} and C_{70} compounds are recovered from the organic solvent.

4. The method according to Claim 3 wherein the separating step comprises evaporating the solvent.

5. The method according to Claim 1 wherein the solvent is benzene or carbon tetrachloride.

6. The method according to any of Claims 1 to 5 wherein the evaporation of graphite is effected by passing high electrical current through graphite rods.

7. The method according to any of Claims 1 to 6 wherein the inert gas is helium or argon.

8. The method according to any of Claims 1 to 7 wherein the graphite is evaporated at pressures ranging from about 50 torr to about 400 torr.

9. The method according to any of Claims 1 to 7 wherein the pressure ranges from about 2 to about 3 atmospheres.

10. The method according to any of Claims 1 to 9 further comprising separating the C_{60} compound from the C_{70} compound.

11. Amorphous or crystalline particulate matter comprised of C_{60} or C_{70} .

1 12. A carbon product comprising a mixture of
C₆₀ and C₇₀.

5 13. A carbon product, the mass spectrum of
which shows a strong peak at mass 720 amu, the infrared
bonds of which have four intense lines at 1424, 1183, 577,
and 528 cm⁻¹, absorption peaks in the UV at 264 and 339
nm, soluble in non-polar organic solvents and sublimates at
a temperature of from about 300° to 400°C.

10 14. A carbon product produced by the process of
any of Claims 1 to 10.

15 15. A formed or molded product comprising C₆₀
or C₇₀.

16 16. The product according to Claim 14 which is
extended in at least one direction.

17 17. A free flowing particulate comprised of C₆₀
or C₇₀.

18 18. Substantially pure C₆₀ or C₇₀.

19 19. A brownish-red carbon allotrope.

20 20. A carbon product, the mass spectrum of
which shows a molecular ion at 840 amu, a broad peak in
the ultraviolet at 216 nm, and soluble in non-polar
organic solvents.

21 21. C₆₀ or C₇₀.

22 22. The vapor of C₆₀ or C₇₀.

25 23. A method of extracting C₆₀ and C₇₀ from a
carbon source containing same which comprises contacting
the carbon source with a non-polar organic solvent.

24 24. A method according to Claim 22 wherein the
C₆₀ and C₇₀ are recovered from the organic solvent.

30 25. A method according to Claim 22 or 23
wherein the solvent is benzene, carbon tetrachloride or
carbon disulfide.

35 26. A method according to Claim 24 wherein a
carbon source containing C₆₀ and C₇₀ is contacted with
benzene and recovering C₆₀ and C₇₀ from the benzene
solution thus formed.

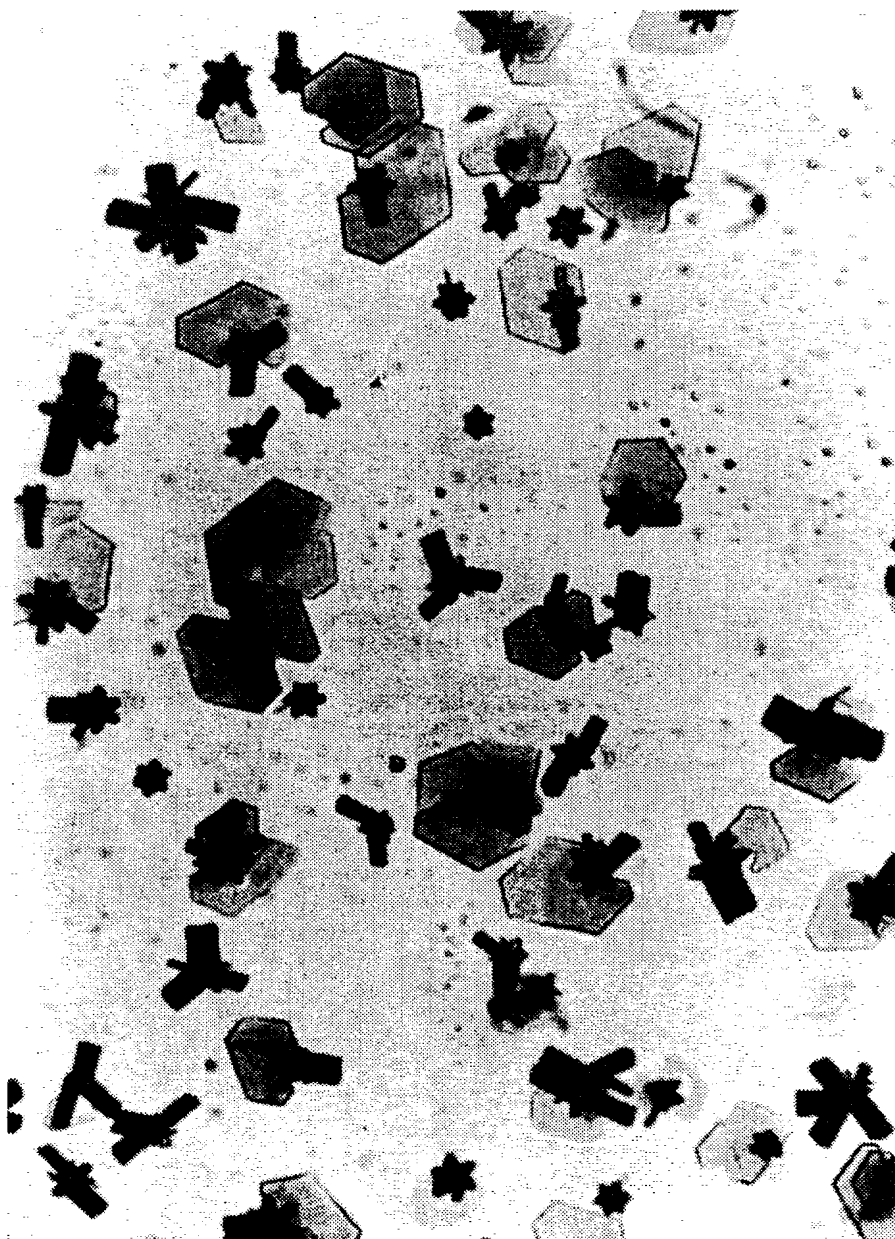


FIG.1

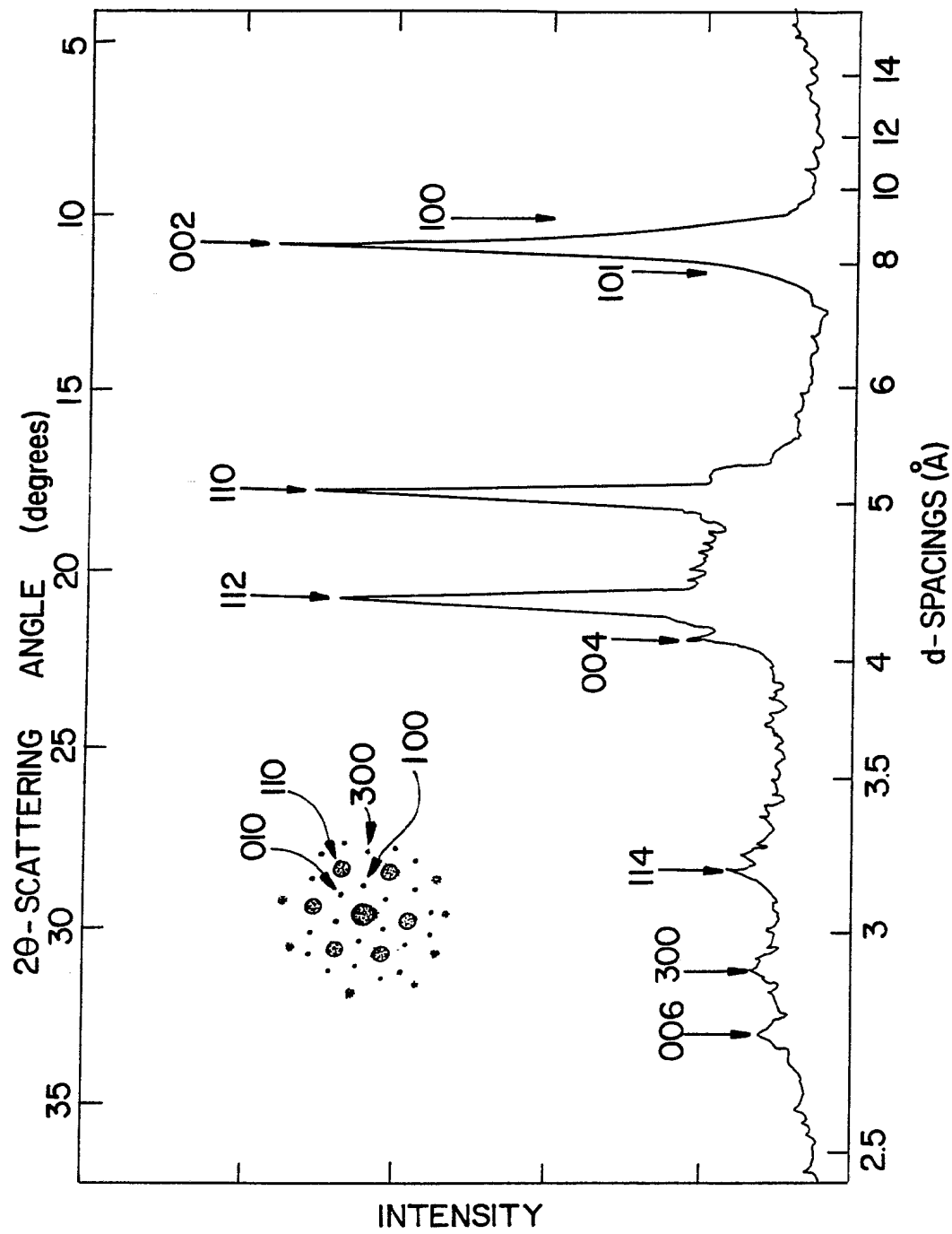


FIG. 2

3/4

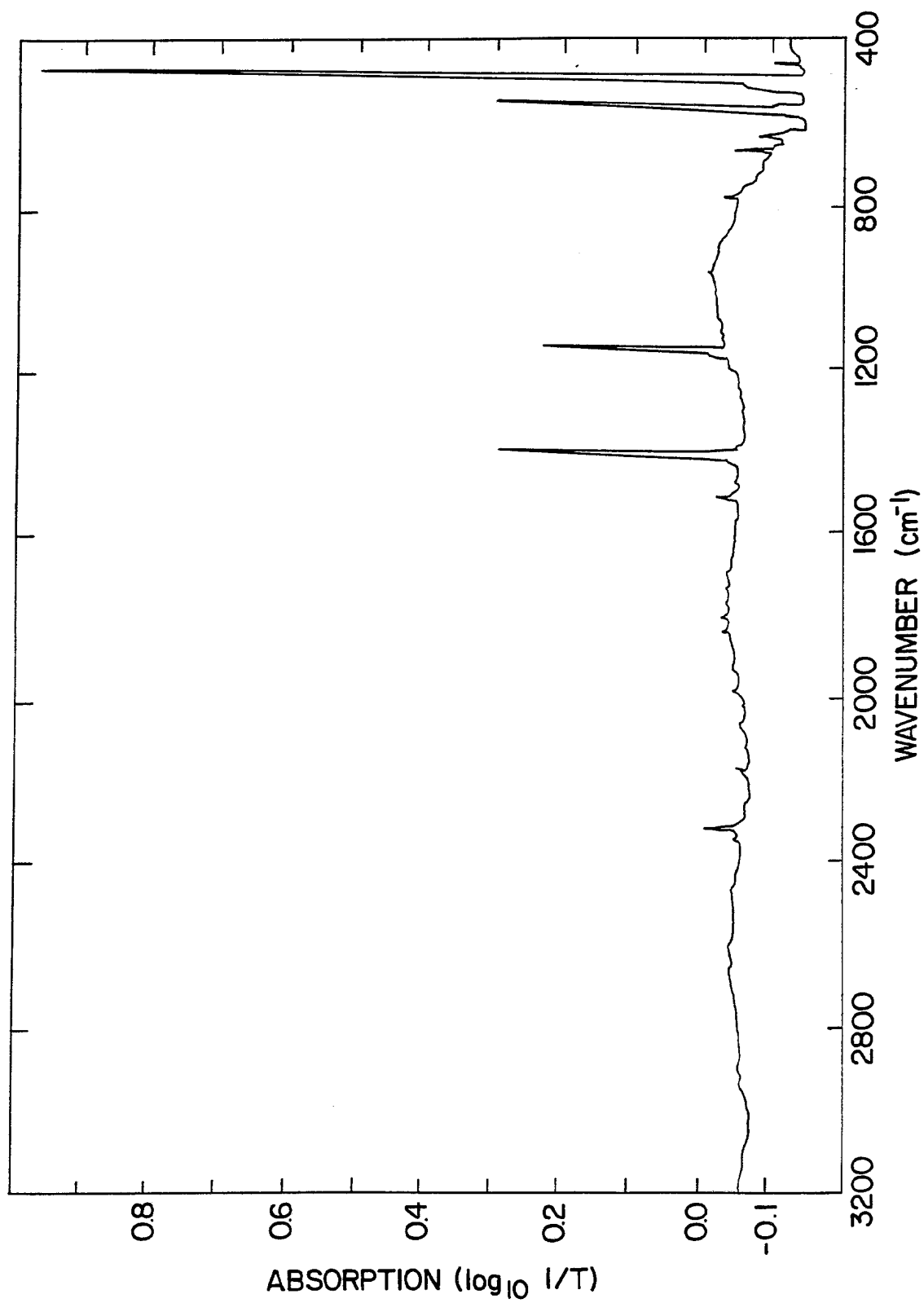


FIG. 3

4/4

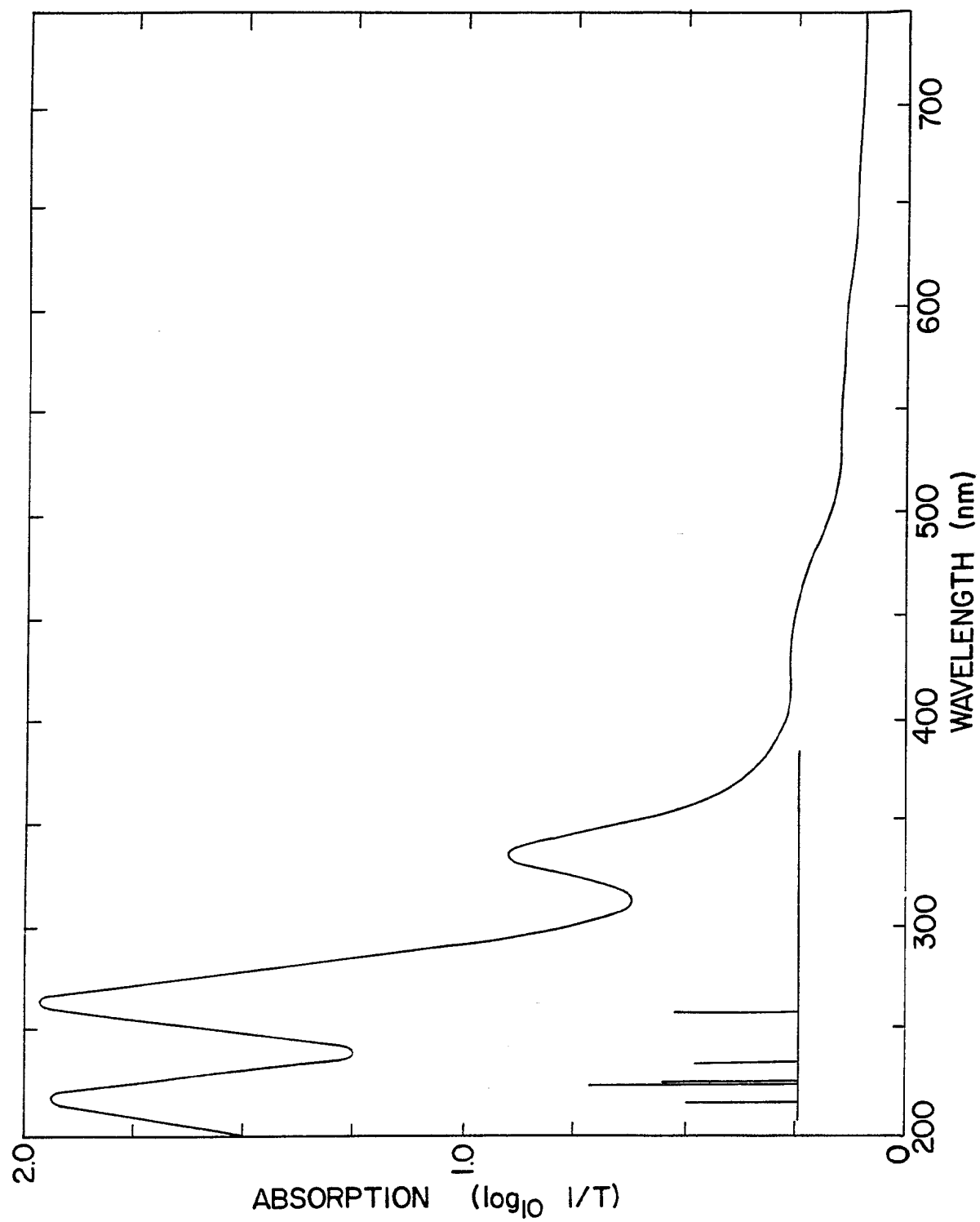
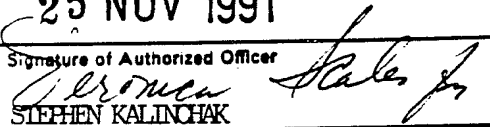


FIG. 4

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/05983

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC 5 : 001B 31/00 U.S. Cl. 423/445B		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
U.S.	423/445, 445B, 449, 460, 658.5, 427/122	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X,Y	US, A, 4,132,671 (DEININGER ET AL) 2 January 1979, See column 2, lines 11-68	23, 25, 26
A	Surface Science, 156, 1985 (KRATSCHMER ET AL) "Spectroscopy of Matrix -Isolated Carbon Cluster Molecules between 200 and 850 nm Wavelength", See pages 814-821.	ALL
X	Nature, 318, 14 November 1985 (KROTO ET AL) "C ₆₀ : Buckminster fullerene", See pages 162-163	11-22
X	Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, Vol. 4, published 1978, by John Wiley & Sons (New York) pages 652-653.	11-22
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
04 NOVEMBER 1991		25 NOV 1991
International Searching Authority		Signature of Authorized Officer
ISA/US		 STEPHEN KALINCHAK

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	<u>Chemical Physics Letters</u> , 137, 4, 19 June 1987 (GERHARDT ET AL) "Polyhedral Carbon Ions in Hydrocarbon Flames" See pages 308-309.	All
A	<u>The Journal of Physical Chemistry</u> , 90, 4, 1988 "Reactivity of Large Carbon Clusters: Spheroidal Carbon Shells and Their Possible Relevance to the Formation and Morphology of Soot", See pages 525-528.	All
T	<u>Scientific American</u> , October 1991 (CURL ET AL) "Fullerenes", See pages 54-63.	11-22
T	<u>Nature</u> , 352, 11 July 1991, (HOWARD ET AL), "Fullerenes C ₆₀ and C ₇₀ in flames", See pages 139-141.	11-22